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Radiocarbon

Disclaimer

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Sub-micron sized airborne particulate matter is not collected well on regular quartz or glass fiber filter papers. We used a micro-orifice uniform deposit impactor (MOUDI) to size fractionate particulate matter (PM) into six size fractions and deposit it on specially designed high purity thin aluminum disks. The MOUDI separated PM into fractions 56-100 nm, 100-180 nm, 180-320 nm, 320-560 nm, 560-1000 nm, and 1000-1800 nm. Since MOUDI have low flow rates, it takes several days to collect sufficient carbon on 47 mm foil disks. The small carbon mass (20-200 microgram C) and large aluminum substrate (~25 mg Al) presents several challenges to production of graphite targets for accelerator mass spectrometry (AMS) analysis. The Al foil consumes large amounts of oxygen as it is heated and tends to melt into quartz combustion tubes, causing gas leaks. We describe sample processing techniques to reliably produce graphitic targets for ^{14}C-AMS analysis of PM deposited on Al impact foils.

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Introduction

Atmospheric particulate matter (PM) is a complex mixture of small particles and liquid droplets in the air produced by natural phenomena and anthropogenic activities. These particles vary in size from nanometers to tens of microns and adversely impact public health, visibility, and produce radiative forcing effects on global climate. Exposure to particulate matter, particularly sub-micron particles inhaled deep into the lungs, in ambient air has been linked to increased aggravated asthma, premature death in people with heart and lung disease, and hospital admission for cardiovascular and respiratory diseases in many urban areas (Dockery 2009; Pope and Dockery 2006).

To protect public health and welfare, the United States Environmental Protection Agency (USEPA) promulgated national ambient air quality standards (NAAQS) for PM_{10} (aerodynamic diameter $\leq$10 μm) in 1987 and for $PM_{2.5}$ (aerodynamic diameter $\leq$2.5 μm) in 1997. These NAAQS established limits for 24-h and annual exposures; 150 $\mu g/m^3$, 24-h average; 50 $\mu g/m^3$, annual average for PM_{10} in 1987 and 65 $\mu g/m^3$, 24-h average; 15 $\mu g/m^3$, annual average for $PM_{2.5}$ in 1997. USEPA revised the NAAQS PM standard in 2006 (USEPA 2006), reducing the 24-h average $PM_{2.5}$ standard from 65 to 35 $\mu g/m^3$ while retaining the annual average $PM_{2.5}$ standard and 24-h average PM_{10} standard. The state of California has set a lower annual average $PM_{2.5}$ standard of 12 $\mu g/m^3$.

The size distribution of anthropogenic produced particles in PM has changed dramatically over the past couple decades. The earliest vehicle emission standards regulated PM mass/distance driven without any constraint on the size of the particles. It was clear that relatively few large particles dominated these measurements. As vehicle and fixed combustion

source PM emission standards tightened over the past couple decades, emission control technology effectively reduced PM mass emitted. The largest particles responsible for most of the mass were easiest to capture and their elimination reduced mass most dramatically. Unfortunately, the emission controls that enabled combustion sources to meet the regulations also produced many more smaller and ultra fine (<100 nm) particles (USEPA 2004; Seigneur 2009). The recent switch to ultra-low sulfur diesel fuel seems to have reduced the number of particles <30nm but not change PM mass (Ristovski 2006).

Capturing the sub-micron sized PM of interest for radiocarbon analyses requires a non-traditional collection system. Standard high volume air samplers typically collect PM_{10} or $PM_{2.5}$ on quartz or glass fiber filters. Glass fiber and quartz filters are efficient collectors of these relatively large particles, but less effective ultrafines. Size separation of ultrafines depends on aerodynamic flow, and the rough surfaces of quartz and glass fiber disrupt air flow. We used a micro-orifice uniform deposit impactor (MOUDI) to size fractionate particulate matter (PM) into six size fractions (56-100 nm, 100-180 nm, 180-320 nm, 320-560 nm, 560-1000 nm, and 1000-1800 nm) and deposit it on specially designed high purity thin aluminium disks. Glass fiber and quartz filters do not work in MOUDI because the relatively rough surface of the filters produces too much turbulence. The aluminum impactor disks capture the smallest particles. They are not filters, the PM is physically implanted onto foil disks.

PM ranging from ultrafines to 2 μm collected on Al impactor disks or strips are not typically analyzed for radiocarbon content. MOUDI have small orifices and low flow rates, typically around 30 L/min, compared to high volume samplers with flow rates >1000 L/min. MOUDI impactor disks are typically analyzed to identify metals or organic compounds found in these tiny particles [Geller et al 2005; Robert et al 2007a; Robert et al 2007b; Kleeman et al

2008; Krudysz et al 2008; Kleeman et al 2009]. The MOUDI samples needed to operate continuously for 3-4 days to deposit sufficient carbon mass for radiocarbon analyses.

Beyond the long collection times required, radiocarbon analyses of Al impactor strips also present challenges in sample preparation and graphite production. Despite the long collection times, most samples contained only 20-50 μg C embedded in 25 mg of Al. We use a pilot collection study as an example of the challenges a set of MOUDI foil disks presents for radiocarbon analysis. The Al foil consumes large amounts of oxygen during sample combustion and the tips of the Al tend to melt into the quartz sample combustion tubes causing leaks. We describe sample processing techniques to reliably produce graphite targets for ^{14}C-AMS analysis of PM deposited on Al impactor disks.

Materials and Methods

Sampling site and collection

The sampling site for this study was the rooftop of a gymnasium at an elementary school in a residential neighborhood in Sacramento, CA. The rooftop is about 10 m above the ground surface and 2.5 km from a major interstate freeway.

Before sample collection, the MOUDI samplers were cleaned using tap water, methanol, and hexane in the laboratory to avoid any possible contamination. Aluminum foil substrates for the MOUDI samplers were pre-combusted at 450 °C for 4 hours and weighed using a microbalance. Pre-weighed 47 mm diameter aluminum substrates were installed on each MOUDI plate in the laboratory and then transported to the sampling site.

The MOUDI samplers used in this study was originally designed to collect atmospheric PM with aerodynamic diameters ranging from 56 nm to 18 μm in 11 different size ranges. They were modified to remove PM larger than 1800 nm using cyclones attached to inlets of the MOUDI sampler and collected six size ranges: 56-100 nm, 100-180 nm, 180-320 nm, 320-560 nm, 560-1000 nm, and 1000-1800 nm. The flow rate was 30 L/min. Sampling spanned multiple days to acquire a sufficient mass of carbon for radiocarbon analysis.

Loaded aluminum foil substrates were transported to the laboratory installed in the MOUDI samplers and removed from each plate and individually placed in Petri dishes lined with aluminum foil. A loaded foil is shown in Figure 1. All Petri dishes were sealed with Teflon tape and stored in a freezer (-20 °C). Loaded disks were transported by ground transportation UC-Davis to Lawrence Livermore National Laboratory for radiocarbon analysis.

AMS sample preparation

The loaded foil disks and control blanks were cut into thin strips (~3 mm) for placement in 6mm O.D. quartz combustion tubes. The foil strips were pushed into the quartz tube with a stainless steel rod and CuO was added after every 2 or 3 strips. Care was taken to avoid forming an impermeable plug of foil when packing with the rod. The distributed CuO oxidizer insured oxygen throughout the tube in case of accidental production of a foil plug. The foil substrate required double-tubing, placing the 6 mm quartz tube inside a 10 mm O.D. quartz tube for combustion (Fig. 2a). The tips and edges of the foil touching the quartz on edge caused the foil to melt and compromise the quartz causing gas leaks. By double-tubing, the inner tube was damaged by the foil melts but the outer tube remained intact. The combustion of the foil yielded a gossamer film aside from the melts at the tips (Fig. 2b). Each sample contained 600-800 mg of CuO to ensure sufficient oxygen to oxidize both the 25 mg Al foil and the 20-200 μg C.

All samples and controls were prepared in the LLNL natural carbon preparation laboratory using established methods. The quartz tubes are evacuated, sealed with a H_2/O_2 torch, and heated to 900 °C for 3.5 hours to oxidize all carbon to CO_2. After each quartz sample tube cooled to room temperature, it is placed in a flexible, evacuated chamber and broken to release the combustion gases. The evolved CO_2 was purified, trapped, and reduced to graphite in the presence of iron catalyst in individual reactors (Vogel et al. 1987; Santos et al 2004). All $^{14}C/C$ measurements were completed with graphite targets analyzed at the Center for Accelerator Mass Spectrometry at Lawrence Livermore National Laboratory on the HVEE FN-class tandem electrostatic AMS system.

Blank foil disks were packaged as described above but contained too little carbon (≤1 μg) to produce a viable AMS sample. Blank disks were then combusted with small measured samples (20-50 μg C) of NIST 4990C oxalic acid or ^{14}C-free fullerene soot to assess fossil and contemporary carbon contributions, respectively, to the background (Brown and Southon, 1997). The foil substrate did not contain any additional contaminating carbon than that from using double-tubes and very large amounts of CuO.

We used a $\delta^{13}C$ correction of –25±2 for all samples based on measurement of selected sample splits of $PM_{2.5}$ samples collected concurrently. Corrections for background contamination introduced during sample preparation were made following the procedures of Brown and Southon (1997). All data were normalized with six identically prepared NIST SRM 4990B (Oxalic Acid I) standards. We used NIST SRM 4990C (Oxalic Acid II), ANU sucrose, and TIRI wood (Scott 2003) as quality controls to monitor spectrometer performance. The measurement error was determined for each sample and ranged between ±2-10‰ (1 SD).

The text reports $^{14}C/C$ concentrations in $F^{14}C$ units (fraction modern) using the nomenclature for reporting post-bomb data (Reimer et al 2004). We avoid the percent modern carbon (pMC) nomenclature due to its inconsistent use in the literature.

Results and Discussion

The contributions of fossil and contemporary carbon for these samples were measured using the technique of Brown and Southon (1997) at 2.0±0.5 and 2.5±0.5 μg C, respectively, for a double-tubed sample possessing 80-200 μg C. These values are consistent for double-tube samples with large amounts of CuO. Only one foil can be placed inside the inner quartz combustion tube. When carbon loading on a foil is <20 μg C, multiple foil disks collected from MOUDI operating in parallel can be combusted individually and the CO_2 combined to produce a single graphite sample. The contributions of fossil and contemporary carbon for two double-tube samples were measured at 4.0±1.0 and 5.0±1.0 μg C, respectively.

The PM <1 μm had high carbon content, typically on the order of 75% C by mass (Fig. 3). This pilot test collected samples during the late autumn when dust levels are relatively low. Still, the 1000-1800 nm fraction had significant mineral content. These carbon masses are useful when assessing whether multiple MOUDI filters are needed to obtain successful graphite targets.

The radiocarbon concentrations of the size-fractionated PM varied with particle size over a relatively narrow range (Fig. 4). The PM was attributed to either fossil or biogenic carbon sources through its radiocarbon concentration. There are obviously more than two carbon sources, but a simple two-component source model addresses the isotopic signatures of major carbon sources. The fossil contribution is produced primarily from fossil fuel combustion, most

commonly assigned to diesel engines and large stationary sources. The biogenic contribution is a mixture of natural processes and anthropogenic activities. Residential wood burning produces high levels of PM with carbon that generally was removed from the atmosphere in the past 10-100 years. Assigning a $^{14}C/C$ value for biogenic carbon requires estimating the age of wood used for residential wood burning. This value will vary with location and the source of firewood. In the case of forest fires, much of the biomass consumed consists of ground cover, brush and leaves grown over the past few years (Bench and Herckes 2004).

With the measurement of total carbon mass (m_T) for every size-fraction, the mass of biogenic (m_B) and fossil (m_F) carbon is easily calculated.

$$m_B + m_F = m_T \quad (1)$$

The ^{14}C of each component is the product of the mass (m_i) and measured isotopic ratio (R_i) of that component. The total ^{14}C is the sum of the parts.

$$R_T m_T = R_F m_F + R_B m_B \quad (2)$$

Equation 1 can be substituted into Eq. 2 and solved for m_F in terms of the measured quantities m_T, R_T, R_B, and R_F. One can then solve for m_B. Figure 4 plots the fossil and biogenic mass contributions for each size-fraction using R_B of $F^{14}C=1.07$ when the atmosphere was about $F^{14}C=1.05$. The fossil carbon contribution was relatively uniform across the size fractions examined. The differences in mass loadings were due to variations in biogenic carbon among the size fractions.

Conclusion

MOUDI Al foil disks are amenable to $^{14}C/C$ analyses to provided fossil and biogenic carbon contributions in sub-micron size-fractionated PM. The Al foil impactor disks used in MOUDI samplers require customized sample processing to insure reliable graphite production. Double-tube combustion is required to prevent tube failure and CuO must be sufficient for combustion of the foil disks. The foil disks contain very low levels of carbon, making background quantitation relatively easy. Double-tube combustion, high levels of CuO to combust the Al foil, and the need multiple combustion tubes to acquire PM from multiple disks all raise backgrounds from typical samples. Background samples should be blanks foils with ^{14}C-free material scaled to the unknown sample masses.

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References

Bench G, Herckes P. 2004. Measurement of contemporary and fossil carbon contents of PM2.5 aerosols: Results from Turtleback Dome, Yosemite National Park. *Environ Sci Technol*. 38(8): 2424-2427.

Brown TA, Southon JR. 1997. Corrections for contamination background in AMS ^{14}C measurements. *Nucl Instrum Methods Phys Res Sect B* 123: 208-213.

Dockery DW. 2009. Health effects of particulate air pollution. *Ann Epidemiol*. 19(4):257-63.

Geller VD, Sardar SB, Phuleria H, Fine PN, Sioutas C. 2005. Measurements of Particle Number and Mass Concentrations and Size Distributions in a Tunnel Environment. *Environ Sci Technol*. 39(22): 8653-63.

Kleeman MJ, Riddle SG, Jakober CA. 2008. Size distribution of particle-phase molecular markers during a severe winter pollution episode. *Environ Sci Technol*. 42(17):6469-75.

Kleeman MJ, Riddle SG, Robert MA, Jakober CA, Fine PM, Hays MD, Schauer JJ, Hannigan MP. 2009. Source apportionment of fine (PM1.8) and ultrafine (PM0.1) airborne particulate matter during a severe winter pollution episode. *Environ Sci Technol*. 43(2):272-279.

Krudysz MA, Froines JR, Fine PM, Sioutas C. 2008. Intra-community spatial variation of size-fractionated PM mass, OC, EC, and trace elements in the Long Beach, CA area. *Atmos Environ* 42(21): 5374-89.

Pope CA, Dockery DW. 2006. Health effects of fine particulate air pollution: lines that connect. *J Air Waste Manag Assoc.* 56:709-742.

Reimer PJ, Brown TA, Reimer RW. 2004. Discussion: reporting and calibration of post-bomb ^{14}C data. *Radiocarbon* 46(3): 1299-1304.

Ristovski ZD, Jayaratne ER, Lim M, Ayoko GA, Morawska L. 2006. Influence of diesel fuel sulfur on nanoparticle emissions from city buses. *Environ Sci Technol*. 40(4): 1314-1320.

Robert MA, VanBergen S, Kleeman MJ, Jakober CA. 2007a. Size and composition distributions of particulate matter emissions: part 1--light-duty gasoline vehicles. *J Air Waste Manag Assoc*. 57(12):1414-28.

Robert MA, VanBergen S, Kleeman MJ, Jakober CA. 2007b. Size and composition distributions of particulate matter emissions: part 2--heavy-duty diesel vehicles. *J Air Waste Manag Assoc*. 57(12):1429-38.

Santos GM, Southon JR, Druffel-Rodrigez K, Griffin S, Mazon M. 2004. Magnesium perchlorate as an alternative water trap in AMS graphite sample preparation: a report on sample preparation at KCCAMS at the University of California, Irvine. *Radiocarbon* 46:165-173.

Scott EM. 2003. The Third International Radiocarbon Intercomparison (TIRI) and the Fourth International Radiocarbon Intercomparison (FIRI) 1990-2002 results, analyses, and conclusions. *Radiocarbon* 45: 135-408.

Seigneur C. 2009. Current understanding of ultrafine particulate matter emitted from mobile sources. *J Air Waste Manag Assoc*. 59(1):3-17.

USEPA. 2004. The Particle Pollution Report: Current Understanding of Air Quality and Emissions through 2003; EPA 454-R-04-002; Monitoring and Analysis Division, Office of Air Quality Planning and Standards Emissions: Research Triangle Park, NC.

USEPA. 2006. Revisions to ambient air monitoring regulations; final rule. Federal Register, Vol. 71, No. 200, 61236-61328, United States Environmental Protection Agency, Washington, DC.

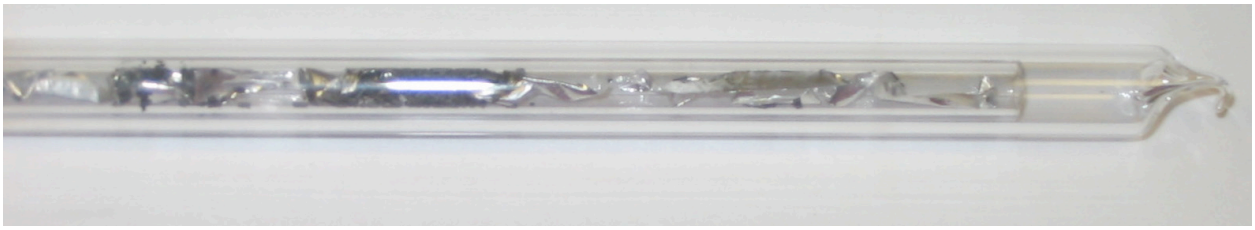
Vogel JS, Southon JR, Nelson DE. 1987. Catalyst and Binder Effects in the Use of Filamentous Graphite for AMS. *Nucl Instrum Methods Phys Res Sect B* 29:50-56.

Captions

Fig. 1. Loaded foil impactor disk for PM 180-320 nm.

Fig. 2. MOUDI foil sample packaged in quartz double-tube before (a) and after (b) combustion.

a



b

Fig. 3. PM loading on MOUDI disks in mass deposited per m^3 of air flow.

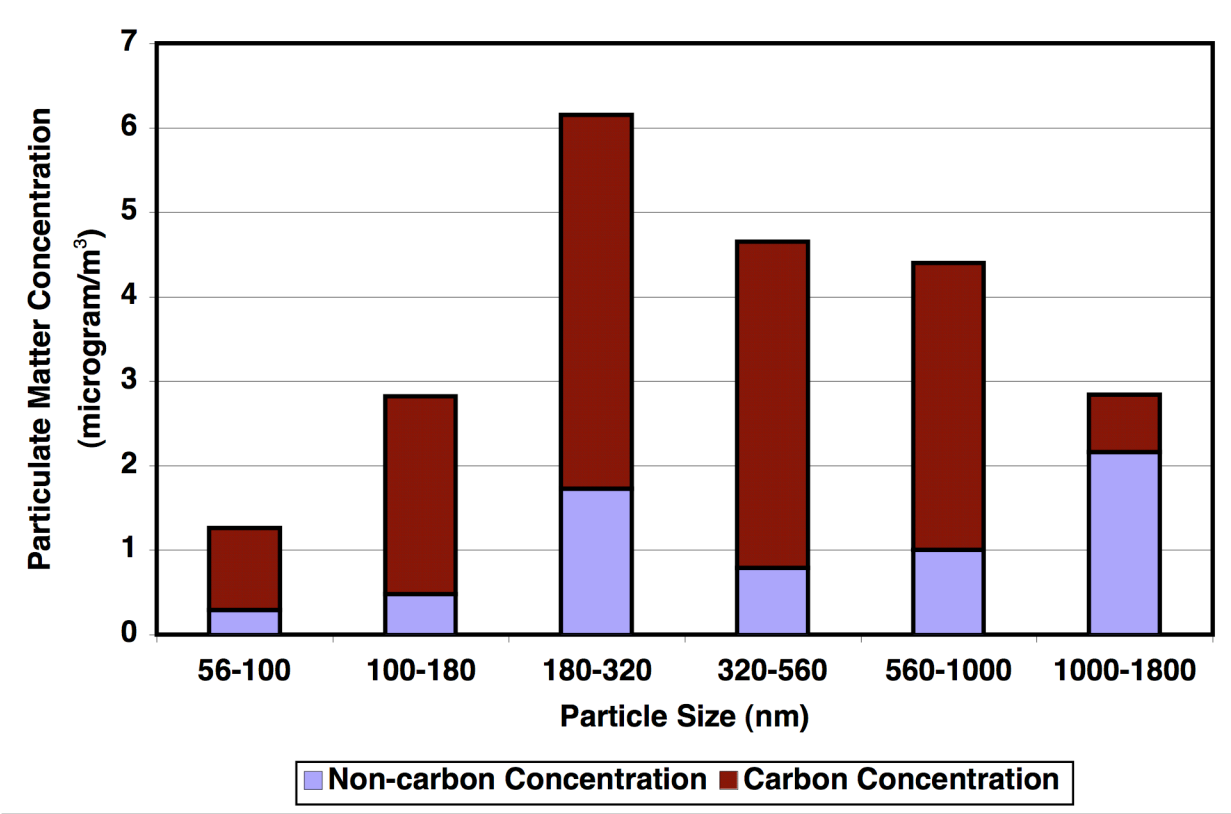


Fig. 4. Contributions of fossil and biogenic carbon to size-fractionated PM. The mass of the fossil carbon contribution changed little among the different size fractions. The varied mass of the biogenic carbon among size fractions produced the variation in measured $^{14}C/C$.